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Measuring Organic Pollutants at Ultra-Trace Levels in the San Francisco Bay

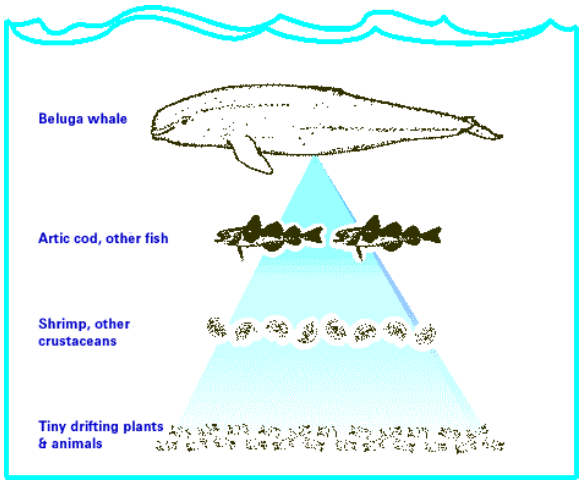
The City of San Jose is one of four San Francisco Bay municipalities participating in the Trace Organic Contaminants in Effluent Study. Palo Alto, Sunnyvale and the Fairfield-Suisun Sewer District are the remaining co-participants. The purpose of this study is to comply with a provision within the National Pollutant Discharge Elimination System (NPDES) permit for the three lower South Bay wastewater treatment plants. (1) The San Francisco Estuary Institute (SFEI) is coordinating the study between the four treatment plants and the contract laboratories as well as maintaining the study's quality assurance program.

Trace organic contaminants include pesticides, PCBs, PAHs and dioxins (and furans) as identified in the California Toxics Rule (CTR) released in 1999. Currently the California State Regional Water Quality Control Board for San Francisco Bay (RWQCB) requires compliance with pollutant concentrations as low as 14x10^-15 grams (14 femtograms) in 1 liter of water or 14 parts per quintillion. (1) This would be the equivalent of about 14 drops of pollutant in 1 million standard 10,000 gallon railroad tank cars.

Many of these pollutants are very persistent in the environment. For example, although production of PCBs in the United States was banned as a result of the Toxics Substances Control Act in 1977, measurable amounts of the pollutants persist in soils and water bodies today. (2) It is estimated that approximately 1.2 billion pounds of PCBs were manufactured in the United States from 1929 until its banning. (3) What's more, PCB's and other pollutants may travel on the wind through the atmosphere, even across continents.

Why are these organic pollutants regulated at such low trace level concentrations?

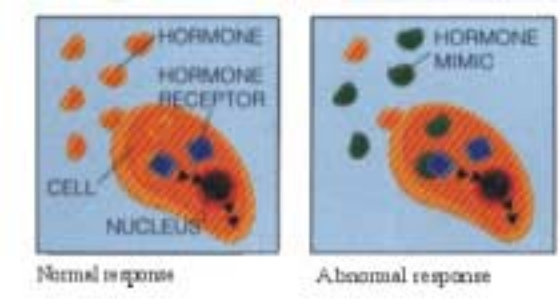
Man-made pollutants are of greater concern if their presence does not diminish naturally in the environment. Furthermore, natural processes like bio-accumulation and bio-magnification concentrate many of these compounds, increasing their threat to living organisms and the environment. Bio-accumulation (concentration by the biological uptake of a compound from solution) and bio-magnification (concentration in organisms higher in the food chain by consumption of organisms lower in the food chain) can result in elevated chemical levels capable of causing health and reproductive problems. These processes affect higher species while those lower in the food chain may remain unaffected. Bio-magnification takes place through successive steps through the food chain, which may involve simple and/or very complex food webs, so defining the magnitude of exposure and consequences to wildlife can be very difficult. The fate and regulation of these compounds continue to be the source of considerable public and scientific debate.



What health problems do these compounds cause?

Two of the most serious problems associated with these compounds are carcinogenesis and endocrine disruption. Carcinogenesis is the ability of a compound to cause cells to reproduce uncontrollably (cancer). Endocrine disruption occurs when pollutant toxins of similar molecular geometry act as hormone mimics, which bind to hormone-receptors in the cell. This can lead to various consequences depending on the endocrine system that has been affected.

PCB's and dioxin are well-known endocrine disrupters and carcinogens. Specifically, these pollutants tend to accumulate in the fatty tissue of the organism and are mobilized at the cellular level when fat stores are metabolized for energy. When higher concentrations are reached, these pollutants can fool the organism's own cellular biochemistry causing genetic mutations and carcinogenesis. (5)



After twenty years of research, the list of compounds that act as endocrine disrupters and carcinogens like PCB's, dioxins and furans has grown large. So far, health effects linked to specific disrupters have been limited to laboratory animals and their offspring. (2)

In 1992 it was discovered that several of the same type of receptors in a cell must be activated in order to trigger carcinogenesis. (2) This implies that we may soon be able to identify exact threshold levels of carcinogenic compounds. This new research may increase or decrease current toxic regulations. In the mean time, the EPA maintains the simpler approach of setting limits based on linear extrapolations from laboratory animals.

In general, uncertainties inherent in the identification of a compound's cancer causing properties have made environmental regulation complex. In the 1950s, U.S. Representative James J. Delaney held a series of legislative hearings and asked a panel of toxicologists if they could predict whether an organic compound would cause cancer in humans. They said, "No" in many cases. Representative Delaney then wrote into the 1958 food safety laws the famous Delaney Clause, which simply states that no compound, which causes cancer should be added to our food. (4) That clause served us well for over thirty years, but today it is somewhat outdated.

The main reason is the amazing increase in the sensitivity of analyses. In the early 1900s, analysts could detect milligram quantities of impurities (10^-3 grams). Around 1950, the limit had fallen to microgram amounts (10^-6 grams). In the 1970s, the detection limits were decreased to nanogram quantities (10^-9 grams). In the same era, picogram (10^-12 grams) quantities could be detected easily. With extensive clean-up and optimization, the limits could be pushed to femtogram (10^-15 grams) quantities. (2)

Lately, articles have appeared in the literature reporting analyses at attogram (10 ^–18 grams) levels. Perhaps the ultimate to date is the claim that High Performance Capillary Electrophoresis (HPCE) is capable of detecting milliattograms (10^-21 grams). Since Avogadro's number is 6 x 10^23 molecules per mole, this sensitivity is very close to counting molecules. (4) As scientists advance the ability to measure pollutants at low levels, it is hoped that our knowledge of environmental impacts will increase to promote successful pollutant reduction strategies and informed regulatory monitoring decisions.

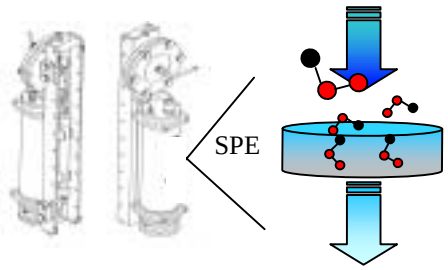
How are organic pollutants collected and measured at ultra-trace levels?

Claims of ultra-trace level detection and quantitation in a controlled laboratory are vastly different from measuring ultra-trace level concentrations in the field environment. Contrary to the laboratory, the field environment is constantly threatened by sources of signal competition known as background. Essentially, the process of detection relies on measuring signal by its separation from the surrounding background or noise. Detection is routinely described as the signal to noise ratio (S/N).

Depending on the background, measuring a signal can be as easy as seeing an elephant in a swimming pool or as difficult as a needle in a haystack. However, when you consider concentration levels of parts per quadrillion (ppq) (1x10^-12 grams in 1-liter of water) or 1 drop of contamination in 1 thousand 10,000 gallon railroad tank cars, additional steps are needed to assure measurement accuracy. For example, in 1995 the EPA drafted EPA Method 1669, which specifically describes methods of sampling known as ultra-clean techniques. These techniques include the use of gloves and other forms of protection, which ensure a level of confidence in reducing sample contamination and/or background noise. Quality checks such as blanks and known spiked concentrations are also employed during sample collection to check measurement performance and signal recovery.

In addition to clean techniques, the laboratory also uses concentration methods, which increase the signal the instrument detects. We should keep in mind though that concentrating the sample also increases the noise by the same factor. The trick is to collect a sample while keeping any contamination and/or background noise to a minimum. Concentrating a 1 liter sample is feasible when measuring 1x10^-6 grams in 1 liter (1 ppb) of water. However, when the concentration drops to 1x10^-15 grams in 1 liter different methods of collection have to be considered. An analysis at this level of sensitivity is known as ultra-trace and requires special techniques of sampling.

One such technique is Solid Phase Extraction or SPE. The principle of SPE includes passing several liters of sample through a resin filter that has organic retention properties. Using this technique, concentrations as low as femtograms (1x10^-15 grams) in 1 liter or parts per quintillion have been measured. With SPE, samples can now be concentrated in the field, which considerably reduces the amount of water required for laboratory concentration methods to reach the ultra-trace level.



Since SPE is a new sampling technique, results from the Trace Organic Contaminants Effluent Study will be evaluated for precision and magnitude between the San Francisco Bay treatment plants. Information from this study will be used to aid Total Maximum Daily Load (TMDL) calculations and future sampling exercises. In addition, information on feasibility and necessary laboratory practices in using this sampling technique will be used to design appropriate regulatory monitoring routines as mandated by the California State Regional Water Quality Control Board.

References

1. State of California, California Regional Water Quality Control Board San Francisco Bay, Cities of San Jose and Santa Clara, San Jose/Santa Clara Water Pollution Control Plant, San Jose, Santa Clara County – NPDES Permit Reissuance, September 17, 1997.

2. Jones, Kenneth, "DIOXIN: A Technical Review", M.P.P. Northeast Center for Comparative Risk [Note 1: Dr. Jones is Assistant to the Director at the Northeast Center for Comparative Risk and is also a research biochemist at the University of Vermont in Burlington, Vermont.], 2000

3. Ramamoorthy, Ramamoorthy, "Chlorinated Organic Compounds in the Environment, Regulatory and Monitoring Assessment", CRC Press, 1997

4. Council for Agricultural Science and Technology, Summary Correspondence on Delaney Clause and Low Detection, 1993

5. Canadian Government Environment Fact Sheet, "Endocrine Disrupting Substances in the Environment", 1999

For additional information on this article or San Jose's involvement in the San Francisco Bay Trace Organic Effluent Study, please contact Eric Hansen at (408) 945-3741, Research Chemist with the Laboratory Division of the Watershed Protection Group.